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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C11D 17/00, 1/29, 1/62, 1/65, 1/37, 3/37</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/06519</b> <b>(43) International Publication Date:</b> 11 February 1999 (11.02.99)
<b>(21) International Application Number:</b> PCT/US98/15281 <b>(22) International Filing Date:</b> 23 July 1998 (23.07.98)  <b>(30) Priority Data:</b> 60/054,099 29 July 1997 (29.07.97) US  <b>(71) Applicant (for all designated States except US):</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> DEPLANCHE, Patrick, Firmin, August [BE/BE]; Dendermondsesteenweg 797, B-9070 Destelbergen (BE). de BUZZACCARINI, Francesco [IT/BE]; Koningin Astridlaan 5, B-2870 Breendonk (BE). FREDJ, Abdennaceur [TN/BE]; Ossegem Straat 103, B-1861 Wolveterm (BE). REDDY, Pramod, Kakumanu [US/US]; 7986 Kingfisher Lane, West Chester, OH 45069 (US). BOSWELL, Robert, Walter [US/US]; 3998 Schroeder Drive, Hamilton, OH 45011 (US). SADOWSKI, Eugene, Steven [US/US]; 9980 Pebbleknoll Drive, Cincinnati, OH 45252 (US).		<b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).  <b>(81) Designated States:</b> BR, CA, CN, IL, JP, MX, TR, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> AQUEOUS, GEL LAUNDRY DETERGENT COMPOSITION  <b>(57) Abstract</b>  The present invention relates to stable, aqueous heavy duty gel laundry detergent compositions comprising anionic surfactants, fatty acids, and specially selected agents to provide exceptional cleaning benefits. The anionic surfactant component comprises alkyl sulfates and alkyl ethoxylated sulfates.		

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## AQUEOUS, GEL LAUNDRY DETERGENT COMPOSITION

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TECHNICAL FIELD

The present invention relates to stable, aqueous heavy duty gel laundry detergent compositions comprising anionic surfactants, fatty acids, and specially selected agents to provide exceptional cleaning benefits. The anionic surfactant component comprises alkyl sulfates and alkyl ethoxylated sulfates.

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BACKGROUND OF THE INVENTION

The art is replete with examples of laundry detergent compositions which have good cleaning properties. Although many of these are liquids, the formulation of gel detergent compositions present numerous problems to the formulator, including high viscosity at pouring shear rate, instability during storage, unacceptable grease cleaning, and undesirable appearance.

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Attempts to formulate gel laundry detergent compositions in the past have included the use of clays or polymers which act to form a shear thinning composition. While these compositions are gels, many have been found to have poor physical product characteristics, including phase split.

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It has now been found that aqueous, heavy duty gel detergent compositions containing certain anionic surfactants and fatty acid surfactants provide excellent cleaning performance and attractive product characteristics, i.e., are structured, phase stable, and have a rheology which allows for easy pouring from the product container.

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Without being limited by theory, it is believed that these novel compositions have an internal structure which comprises a planar lamellar phase. The presence of such a phase in detergent compositions may be determined by optical or electron microscopy.

SUMMARY OF THE INVENTION

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It is an object of the invention herein to provide an aqueous heavy duty gel laundry detergent composition which provides excellent cleaning and a desirable rheology.

The present invention encompasses a heavy duty gel laundry detergent compositions comprising, by weight of the composition:

- 35 a) from about 15% to about 40% of an anionic surfactant component which comprises, by weight of the composition:
- (i) from about 5% to about 25% of alkyl polyethoxylate sulfates wherein the alkyl group contains from about 10 to about 22 carbon atoms and the polyethoxylate chain contains from 0.5 to about 15, preferably from 40 0.5 to about 5, more preferably from 0.5 to about 4, ethylene oxide moieties; and
- (ii) from about 5% to about 20% of fatty acids; and
- b) and one or more of the following ingredients: deterative amine, modified polyamine, polyamide-polyamine, polyethoxylated-polyamine polymers, 45 quaternary ammonium surfactants, suitable electrolyte or acid equivalents thereof, and mixtures thereof.

The compositions herein may further contain one or more additional deterative additives selected from the group consisting of non-citrate builders, optical brighteners, soil release polymers, dye transfer inhibitors, polymeric dispersing agents, enzymes, suds 50 suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, antiredeposition agents, antifading agent, dye fixative agents, prill/fuzzing reducing agents, and mixtures thereof.

The compositions herein have a viscosity at  $20 \text{ s}^{-1}$  shear rate of from about 100 cp to about 4,000 cp, preferably from about 300 cp to about 3,000 cp, more preferably from about 500 cp to about 2,000 cp and are stable upon storage.

55 All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius ( $^{\circ}\text{C}$ ) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

#### DETAILED DESCRIPTION OF THE INVENTION

60 In accordance with the present invention, it has now been found that a stable, aqueous heavy duty gel detergent composition is surprisingly formed when certain anionic surfactants and fatty acid surfactants are combined in relative proportions specified hereinafter.

The compositions herein are structured and have a specific rheology. The rheology can be modeled by the following formula:

65 
$$\eta = \eta_0 + K\dot{\gamma}^{(n-1)}$$

where  $\eta$  is the viscosity of the liquid at a given shear rate,  $\eta_0$  is the viscosity at infinite shear rate,  $\dot{\gamma}$  is the shear rate,  $n$  is the shear rate index, and  $K$  is the consistency index. As used herein, the term "structured" indicates a heavy duty

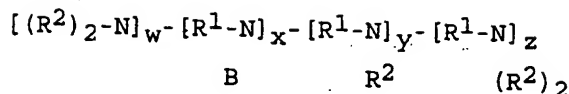
liquid composition having a liquid crystalline lamellar phase and an infinite shear  
viscosity ( $\eta_0$ ) value between 0 and about 3,000cp (centipoise), a shear index ( $n$ )  
value of less than about 0.6, a consistency index value,  $K$ , of above about 1,000,  
and a viscosity ( $\eta$ ) measured at  $20\text{ s}^{-1}$  of less than about 10,000cp, preferably less  
than about 5,000cp. Under low stress levels, a "zero shear" viscosity is above  
about 100,000cp wherein "zero shear" is meant a shear rate of  $0.001\text{ s}^{-1}$  or less.  
The yield value of the compositions herein, obtained by plotting viscosity versus  
stress, is larger than 0.2Pa. These rheology parameters can be measured with any  
commercially available rheometer, such as the Carrimed CSL 100 model.

The compositions herein are clear or translucent, i.e. not opaque.

Electrolytes - Without being limited by theory, it is believed that the presence  
of electrolytes acts to control the viscosity of the gel compositions. Thus, the gel  
nature of the compositions herein are affected by the choice of surfactants and by  
the amount of electrolytes present. In preferred embodiments herein, the  
compositions will further comprise from 0% to about 10%, more preferably from  
about 1% to about 8%, even more preferably from about 2% to about 6%, of a  
suitable electrolyte or acid equivalent thereof. Sodium citrate is a highly preferred  
electrolyte for use herein.

The compositions herein may optionally contain from about 0% to about  
10%, by weight, of solvents and hydrotropes. Without being limited by theory, it is  
believed that the presence of solvents and hydrotropes can affect the structured  
versus isotropic nature of the compositions; By "solvent" is meant the commonly  
used solvents in the detergent industry, including alkyl monoalcohol, di-, and tri-  
alcohols, ethylene glycol, propylene glycol, propanediol, ethanediol, glycerine, etc.  
By "hydrotrope" is meant the commonly used hydrotropes in the detergent industry,  
including short chain surfactants that help solubilize other surfactants. Other  
examples of hydrotropes include cumene, xylene, or toluene sulfonate, urea, C<sub>8</sub> or  
shorter chain alkyl carboxylates, and C<sub>8</sub> or shorter chain alkyl sulfate and  
ethoxylated sulfates.

Modified polyamine - The compositions herein may comprise at least about 0.05%,  
preferably from about 0.05% to about 3%, by weight, of a water-soluble or dispersible,  
modified polyamine agent, said agent comprising a polyamine backbone corresponding to  
the formula:



105 wherein each  $R^1$  is independently  $C_2$ - $C_5$  alkylene, alkenylene or arylene; each  $R^2$  is independently H, or a moiety of formula  $OH[(CH_2)_xO]_n$ , wherein x is from about 1 to about 8 and n is from about 10 to about 50; w is 0 or 1;  $x+y+z$  is from about 5 to about 30; and B represents a continuation of this structure by branching; and wherein said polyamine before alkylation has an average molecular weight of from about 300 to about 1,200.

110 In preferred embodiments,  $R^1$  is  $C_2$ - $C_4$  alkylene, more preferably ethylene;  $R^2$  is  $OH[CH_2CH_2O]_n$ , wherein n is from about 15 to about 30, more preferably n is about 20. The average Molecular Weight of the polyamine before alkylation is from about 300 to about 1200, more preferably from about 500 to about 900, still more preferably from about 600 to about 700, even more preferably from about 600 to about 650.

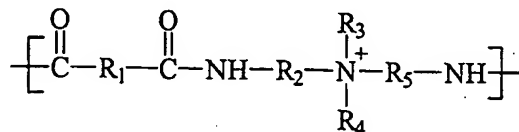
115 In another preferred embodiment,  $R^1$  is  $C_2$ - $C_4$  alkylene, more preferably ethylene;  $R^2$  is  $OH[CH_2CH_2O]_n$ , wherein n is from about 10 to about 20, more preferably n is about 15. The average Molecular Weight of the polyamine before alkylation is from about 100 to about 300, more preferably from about 150 to about 250, even more preferably from about 180 to about 200.

120

Polyamide-Polyamines - The polyamide-polyamines useful herein will generally comprise from about 0.1% to 8% by the weight of the composition. More preferably, such polyamide-polyamine materials will comprise from about 0.5% to 4% by weight of the compositions herein. Most preferably, these polyamide-polyamines will comprise from about 1% to 3% by weight of the composition.

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The polyamide-polyamine materials used in this invention are those which have repeating, substituted amido-amine units which correspond to the general Structural Formula No. I as follows:



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#### Structural Formula No. I

In Structural Formula No. I,  $R_1$ ,  $R_2$  and  $R_5$  are each independently  $C_{1-4}$  alkylene,  $C_{1-4}$  alkaryl or arylene. It is also possible to eliminate  $R_1$  entirely so that the polyamide-polyamine is derived from oxalic acid.

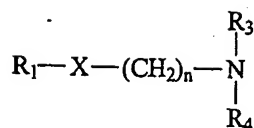
Also in Structural Formula No. I, R<sub>3</sub> is H, epichlorohydrin, an azetidinium group, an  
135 epoxypropyl group or a dimethylaminohydroxypropyl group, and R<sub>4</sub> can be H, C<sub>1-4</sub> alkyl,  
C<sub>1-4</sub> alkaryl, or aryl. R<sub>4</sub> may also be any of the foregoing groups condensed with C<sub>1-4</sub>  
alkylene oxide.

R<sub>1</sub> is preferably butylene, and R<sub>2</sub> and R<sub>5</sub> are preferably ethylene. R<sub>3</sub> is preferably  
epichlorohydrin. R<sub>4</sub> is preferably H.

140 The polyamide-polyamine materials useful herein can be prepared by reacting  
polyamines such as diethylenetriamine, triethylenetetraamine, tetraethylenepentamine or  
dipropylenetriamine with C<sub>2</sub>-C<sub>12</sub> dicarboxylic acids such as oxalic, succinic, glutaric,  
adipic and diglycolic acids. Such materials may then be further derivatized by reaction  
with, for example, epichlorohydrin. Preparation of such materials is described in greater  
145 detail in Keim, U.S. Patent 2,296,116, Issued February 23, 1960; Keim, U.S. Patent  
2,296,154, Issued February 23, 1960 and Keim, U.S. Patent 3,332,901, Issued July 25,  
1967.

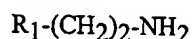
The polyamide-polyamine agents preferred for use herein are commercially  
marketed by Hercules, Inc. under the tradename Kymene<sup>®</sup>. Especially useful are Kymene  
150 557H<sup>®</sup> and Kymene 557LX<sup>®</sup> which are epichlorohydrin adducts of polyamide-  
polyamines which are the reaction products of diethylenetriamine and adipic acid. Other  
suitable materials are those marketed by Hercules under the tradenames Reten<sup>®</sup> and  
Delsette<sup>®</sup>, and by Sandoz under the tradename Cartaretin<sup>®</sup>. These polyamide-polyamine  
materials are marketed in the form of aqueous suspensions of the polymeric material  
155 containing, for example, about 12.5% by weight of solids.

Detersive Amine - Suitable amine surfactants for use herein include detersive amines  
according to the formula:

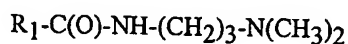


wherein  $R_1$  is a  $C_6$ - $C_{12}$  alkyl group;  $n$  is from about 2 to about 4,  $X$  is a bridging group  
 160 which is selected from  $NH$ ,  $CONH$ ,  $COO$ , or  $O$  or  $X$  can be absent; and  $R_3$  and  $R_4$  are  
 individually selected from  $H$ ,  $C_1$ - $C_4$  alkyl, or  $(CH_2-CH_2-O(R_5))$  wherein  $R_5$  is  $H$  or  
 methyl.

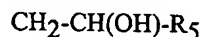
Preferred amines include the following:



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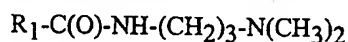


170



wherein  $R_1$  is a  $C_6$ - $C_{12}$  alkyl group and  $R_5$  is  $H$  or  $CH_3$ .

175 In a highly preferred embodiment, the amine is described by the formula:

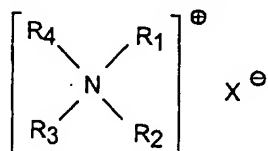


wherein  $R_1$  is  $C_8$ - $C_{12}$  alkyl.

Particularly preferred amines include those selected from the group consisting of  
 octyl amine, hexyl amine, decyl amine, dodecyl amine,  $C_8$ - $C_{12}$  bis(hydroxyethyl)amine,  
 180  $C_8$ - $C_{12}$  bis(hydroxyisopropyl)amine, and  $C_8$ - $C_{12}$  amido-propyl dimethyl amine, and  
 mixtures.

If utilized the deterative amines comprise from about 0.1% to about 10%, preferably  
 from about 0.5% to about 5%, by weight of the composition.

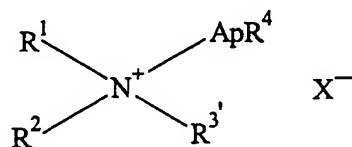
Quaternary Ammonium Surfactants - from about 1% to about 6% of a  
 185 quaternary ammonium surfactant having the formula



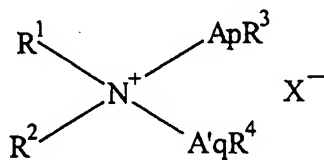
wherein  $R_1$  and  $R_2$  are individually selected from the group consisting of  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  hydroxy alkyl, benzyl, and  $-(C_2H_4O)_xH$  where  $x$  has a value from about 2 to about 5;  $X$  is an anion; and (1)  $R_3$  and  $R_4$  are each a  $C_6$ - $C_{14}$  alkyl or (2)  $R_3$  is a  $C_6$ - $C_{18}$  alkyl, and  $R_4$  is selected from the group consisting of  $C_1$ - $C_{10}$  alkyl,  $C_1$ - $C_{10}$  hydroxy alkyl, benzyl, and  $-(C_2H_4O)_xH$  where  $x$  has a value from 2 to 5;

Preferred quaternary ammonium surfactants are the chloride, bromide, and methylsulfate salts. Examples of preferred mono-long chain alkyl quaternary ammonium surfactants are those wherein  $R_1$ ,  $R_2$ , and  $R_4$  are each methyl and  $R_3$  is a  $C_8$ - $C_{16}$  alkyl; or wherein  $R_3$  is  $C_8$ - $C_{18}$  alkyl and  $R_1$ ,  $R_2$ , and  $R_4$  are selected from methyl and hydroxy-alkyl moieties. Lauryl trimethyl ammonium chloride, myristyl trimethyl ammonium chloride, palmityl trimethyl ammonium chloride, coconut trimethylammonium chloride, coconut trimethylammonium methylsulfate, coconut dimethyl-monohydroxyethyl-ammonium chloride, coconut dimethyl-monohydroxyethylammonium methylsulfate, steryl dimethyl-monohydroxy-ethylammonium chloride, steryl dimethylmonohydroxy-ethylammonium methylsulfate, di-  $C_{12}$ - $C_{14}$  alkyl dimethyl ammonium chloride, and mixtures thereof are particularly preferred. ADOGEN 412™, a lauryl trimethyl ammonium chloride commercially available from Witco, is also preferred. Even more highly preferred are the lauryl trimethyl ammonium chloride and myristyl trimethyl ammonium chloride.

Alkoxylated quaternary ammonium (AQA) surfactants useful in the present invention are of the general formula:



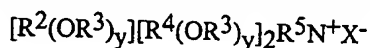
I



II

215 wherein  $R^1$  is an alkyl or alkenyl moiety containing from about 8 to about 18 carbon atoms, preferably 10 to about 16 carbon atoms, most preferably from about 10 to about 14 carbon atoms;  $R^2$  and  $R^{3'}$  are each independently alkyl groups containing from one to about three carbon atoms, preferably methyl;  $R^3$  and  $R^4$  can vary independently and are selected from hydrogen (preferred), methyl and ethyl,  $X^-$  is an anion such as chloride, bromide, 220 methylsulfate, sulfate, or the like, to provide electrical neutrality; A is selected from  $C_1$ - $C_4$  alkoxy, especially ethoxy (i.e.,  $-\text{CH}_2\text{CH}_2\text{O}-$ ), propoxy, butoxy and mixtures thereof; and for formula I, p is from 2 to about 30, preferably 2 to about 15, most preferably 2 to about 8; and for formula II, p is from 1 to about 30, preferably 1 to about 4 and q is from 1 to about 30, preferably 1 to about 4, and most preferably both p and q are 1.

225 Other quaternary surfactants include the ammonium surfactants such as alkyldimethylammonium halogenides, and those surfactants having the formula:



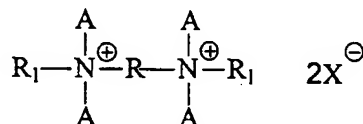
wherein  $R^2$  is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each  $R^3$  is selected from the group consisting of  $-\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_3)-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_2\text{OH})-$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ , and mixtures thereof; each  $R^4$  is 230 selected from the group consisting of  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  hydroxyalkyl, benzyl, ring structures formed by joining the two  $R^4$  groups,  $-\text{CH}_2\text{CHOHCHOH}\text{COR}^6\text{CHOH}-\text{CH}_2\text{OH}$  wherein  $R^6$  is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0;  $R^5$  is the same as  $R^4$  or is an alkyl chain wherein the 235 total number of carbon atoms of  $R^2$  plus  $R^5$  is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Polyethoxylated-Polyamine Polymers - Another polymer dispersant form use herein includes polyethoxylated-polyamine polymers (PPP). The preferred polyethoxylated-polyamines useful herein are generally polyalkyleneamines (PAA's), polyalkyleneimines (PAI's), preferably polyethyleneamine (PEA's), polyethyleneimines (PEI's). A common 240 polyalkyleneamine (PAA) is tetrabutylene pentamine. PEA's are obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly 245 nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See

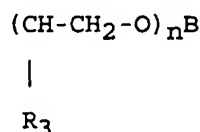
U.S. Patent 2,792,372, Dickinson, issued May 14, 1957, which describes the preparation of PEA's.

- 250 Polyethoxylated polyamines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951

Optionally, but preferred polyethoxyated-polyamine polymers useful for this invention are alkoxyated quaternary diamines of the general formula:

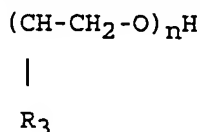


- 260 where R is selected from linear or branched C<sub>2</sub>-C<sub>12</sub> alkylene, C<sub>3</sub>-C<sub>12</sub> hydroxyalkylene, C<sub>4</sub>-C<sub>12</sub> dihydroxyalkylene, C<sub>8</sub>-C<sub>12</sub> dialkylarylene, [(CH<sub>2</sub>CH<sub>2</sub>O)<sub>q</sub>CH<sub>2</sub>CH<sub>2</sub>]- and -CH<sub>2</sub>CH(OH)CH<sub>2</sub>O-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>q</sub>CH<sub>2</sub>CH(OH)CH<sub>2</sub>]- where q is from about 1 to about 100. Each R<sub>1</sub> is independently selected from C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>7</sub>-C<sub>12</sub> alkylaryl, or A. A is of the formula:



- 270 where R<sub>3</sub> is selected from H or C<sub>1</sub>-C<sub>3</sub> alkyl, n is from about 5 to about 100, and B is selected from H, C<sub>1</sub>-C<sub>4</sub> alkyl, acetyl, or benzoyl; X is a water soluble anion.

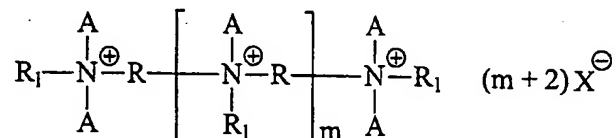
In preferred embodiments, R is selected from C<sub>4</sub> to C<sub>8</sub> alkylene, R<sub>1</sub> is selected from C<sub>1</sub>-C<sub>2</sub> alkyl or C<sub>2</sub>-C<sub>3</sub> hydroxyalkyl, and A is:



- 275 where R<sub>3</sub> is selected from H or methyl, and n is from about 10 to about 50.

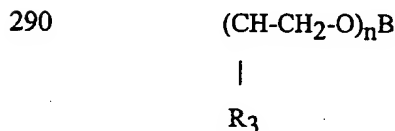
In another preferred embodiment R is linear or branched C<sub>6</sub>, R<sub>1</sub> is methyl, R<sub>3</sub> is H, and n is from about 20 to about 50.

Additional alkoxyated quaternary polyamine dispersants which can be used in the  
 280 present invention are of the general formula:



where R is selected from linear or branched C<sub>2</sub>-C<sub>12</sub> alkylene, C<sub>3</sub>-C<sub>12</sub> hydroxyalkylene, C<sub>4</sub>-C<sub>12</sub> dihydroxyalkylene, C<sub>8</sub>-C<sub>12</sub> dialkylarylene, [(CH<sub>2</sub>CH<sub>2</sub>O)<sub>q</sub>CH<sub>2</sub>CH<sub>2</sub>]- and -  
 285 CH<sub>2</sub>CH(OH)CH<sub>2</sub>O-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>q</sub>CH<sub>2</sub>CH(OH)CH<sub>2</sub>]- where q is from about 1 to about 100. If present, Each R<sub>1</sub> is independently selected from C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>7</sub>-C<sub>12</sub> alkylaryl, or A. R<sub>1</sub> may be absent on some nitrogens; however, at least three nitrogens must be quaternized.

A is of the formula:



where R<sub>3</sub> is selected from H or C<sub>1</sub>-C<sub>3</sub> alkyl, n is from about 5 to about 100 and B is selected from H, C<sub>1</sub>-C<sub>4</sub> alkyl, acetyl, or benzoyl; m is from about 0 to about 4, and X is a  
 295 water soluble anion.

In preferred embodiments, R is selected from C<sub>4</sub> to C<sub>8</sub> alkylene, R<sub>1</sub> is selected from C<sub>1</sub>-C<sub>2</sub> alkyl or C<sub>2</sub>-C<sub>3</sub> hydroxyalkyl, and A is:



where R<sub>3</sub> is selected from H or methyl, and n is from about 10 to about 50; and m is 1.

In another preferred embodiment R is linear or branched C<sub>6</sub>, R<sub>1</sub> is methyl, R<sub>3</sub> is H, and n is from about 20 to about 50, and m is 1.

The levels of these polyethoxylated-polyamine polymers used can range from about  
 305 0.1% to about 10%, typically from about 0.4% to about 5%, by weight. These polyethoxylated-polyamine polymers can be synthesized following the methods outline in U.S. Patent No. 4,664,848, or other ways known to those skilled in the art.

Anionic Surfactant - The anionic surfactant component contains alkyl  
310 polyethoxylate sulfates and may contain other non-soap anionic surfactants or  
mixtures thereof.

Generally speaking, anionic surfactants useful herein are disclosed in U.S.  
Patent No. 4,285,841, Barrat et al, issued August 25, 1981, and in U.S. Patent No.  
3,919,678, Laughlin et al, issued December 30, 1975, both incorporated herein by  
315 reference.

Useful anionic surfactants include the water-soluble salts, particularly the  
alkali metal, ammonium and alkylammonium (e.g., monoethanolammonium or  
triethanolammonium) salts, of organic sulfuric reaction products having in their  
molecular structure an alkyl group containing from about 10 to about 20 carbon  
320 atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl"  
is the alkyl portion of aryl groups.) Examples of this group of synthetic surfactants  
are the alkyl sulfates, especially those obtained by sulfating the higher alcohols  
(C<sub>8</sub>-C<sub>18</sub> carbon atoms) such as those produced by reducing the glycerides of tallow  
or coconut oil. Especially valuable are linear straight chain alkylbenzene  
325 sulfonates in which the average number of carbon atoms in the alkyl group is from  
about 11 to 13, abbreviated as C<sub>11</sub>-C<sub>13</sub>LAS.

Other anionic surfactants herein are the water-soluble salts of alkyl phenol  
ethylene oxide ether sulfates containing from about 1 to about 4 units of ethylene  
oxide per molecule and from about 8 to about 12 carbon atoms in the alkyl group.

330 Other useful anionic surfactants herein include the water-soluble salts of  
esters of  $\alpha$ -sulfonated fatty acids containing from about 6 to 20 carbon atoms in the  
fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-  
soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9  
carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the  
335 alkane moiety; water-soluble salts of olefin sulfonates containing from about 12 to  
24 carbon atoms; and  $\beta$ -alkyloxy alkane sulfonates containing from about 1 to 3  
carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane  
moiety.

The alkyl polyethoxylate sulfates useful herein are of the formula

340 
$$RO(C_2H_4O)_xSO_3^-M^+$$

wherein R is an alkyl chain having from about 10 to about 22 carbon atoms,  
saturated or unsaturated, M is a cation which makes the compound water-soluble,

especially an alkali metal, ammonium or substituted ammonium cation, and x averages from about 0.5 to about 15.

345 Preferred alkyl sulfate surfactants are the non-ethoxylated C<sub>12-15</sub> primary and secondary alkyl sulfates. Under cold water washing conditions, i.e., less than about 65°F (18.3°C), it is preferred that there be a mixture of such ethoxylated and non-ethoxylated alkyl sulfates.

Fatty Acids - Moreover, the anionic surfactant component herein comprises 350 fatty acids. These include saturated and/or unsaturated fatty acids obtained from natural sources or synthetically prepared. Examples of fatty acids include capric, lauric, myristic, palmitic, stearic, arachidic, and behenic acid. Other fatty acids include palmitoleic, oleic, linoleic, linolenic, and ricinoleic acid.

Nonionic Detergent Surfactants - Suitable nonionic detergent surfactants are 355 generally disclosed in U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, and U.S. Patent No. 4,285,841, Barrat et al, issued August 25, 1981. Exemplary, non-limiting classes of useful nonionic surfactants include: C<sub>8</sub>-C<sub>18</sub> alkyl ethoxylates ("AE"), with EO about 1-22, including the so-called narrow peaked alkyl ethoxylates and C<sub>6</sub>-C<sub>12</sub> alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), alkyl dialkyl 360 amine oxide, alkanoyl glucose amide, and mixtures thereof.

If nonionic surfactants are used, the compositions of the present invention will preferably contain up to about 10%, preferably from 0% to about 5%, more preferably from 0% to about 3%, by weight of a nonionic surfactant. Preferred are the ethoxylated alcohols and ethoxylated alkyl phenols of the formula 365  $R(OC_2H_4)_nOH$ , wherein R is selected from the group consisting of aliphatic hydrocarbon radicals containing from about 8 to about 15 carbon atoms and alkyl phenyl radicals in which the alkyl groups contain from about 8 to about 12 carbon atoms, and the average value of n is from about 5 to about 15. These surfactants are more fully described in U.S. Patent No. 4,284,532, Leikhim et al, issued August 370 18, 1981. Particularly preferred are ethoxylated alcohols having an average of from about 10 to about 15 carbon atoms in the alcohol and an average degree of ethoxylation of from about 6 to about 12 moles of ethylene oxide per mole of alcohol.

Other nonionic surfactants for use herein include:

375 The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols. In general, the polyethylene oxide condensates are preferred. These compounds

include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 12 carbon atoms in either a straight chain or branched chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 5 to about 25 moles of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Igepal® CO-630, marketed by the GAF Corporation; and Triton® X-45, X-114, X-100, and X-102, all marketed by the Rohm & Haas Company. These compounds are commonly referred to as alkyl phenol alkoxylates, (e.g., alkyl phenol ethoxylates).

The condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 10 to about 20 carbon atoms with from about 2 to about 18 moles of ethylene oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type include Tergitol® 15-S-9 (the condensation product of C<sub>11</sub>-C<sub>15</sub> linear secondary alcohol with 9 moles ethylene oxide), Tergitol® 24-L-6 NMW (the condensation product of C<sub>12</sub>-C<sub>14</sub> primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol® 45-9 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 9 moles of ethylene oxide), Neodol® 23-6.5 (the condensation product of C<sub>12</sub>-C<sub>13</sub> linear alcohol with 6.5 moles of ethylene oxide), Neodol® 45-7 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 7 moles of ethylene oxide), Neodol® 45-4 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 4 moles of ethylene oxide), marketed by Shell Chemical Company, and Kyro® EOB (the condensation product of C<sub>13</sub>-C<sub>15</sub> alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company. Other commercially available nonionic surfactants include Dobanol 91-8® marketed by Shell Chemical Co. and Genapol UD-080® marketed by Hoechst. This category of nonionic surfactant is referred to generally as "alkyl ethoxylates."

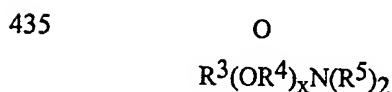
The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of these compounds preferably has a molecular weight of from about 1500 to about 1800 and exhibits water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is

about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available Pluronic® surfactants, marketed by BASF.

415 The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product  
420 contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic® compounds, marketed by BASF.

Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about  
425 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing  
430 one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula



wherein R<sup>3</sup> is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R<sup>4</sup> is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about  
440 3; and each R<sup>5</sup> is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R<sup>5</sup> groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C<sub>10</sub>-C<sub>18</sub> alkyl dimethyl amine  
 445 oxides and C<sub>8</sub>-C<sub>12</sub> alkoxy ethyl dihydroxy ethyl amine oxides.

Alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21,  
 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms,  
 preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a  
 polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from  
 450 about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any  
 reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose  
 and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the  
 hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or  
 galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g.,  
 455 between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6-  
 positions on the preceding saccharide units.

Optionally, and less desirably, there can be a polyalkylene-oxide chain joining the  
 hydrophobic moiety and the polysaccharide moiety. The preferred alkyleneoxide is  
 ethylene oxide. Typical hydrophobic groups include alkyl groups, either saturated or  
 460 unsaturated, branched or unbranched containing from about 8 to about 18, preferably from  
 about 10 to about 16, carbon atoms. Preferably, the alkyl group is a straight chain saturated  
 alkyl group. The alkyl group can contain up to about 3 hydroxy groups and/or the  
 polyalkyleneoxide chain can contain up to about 10, preferably less than 5, alkyleneoxide  
 moieties. Suitable alkyl polysaccharides are octyl, nonyl, decyl, undecyl, dodecyl, tridecyl,  
 465 tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-, tri-, tetra-, penta-, and  
 hexagluco-sides, galactosides, lactosides, glucoses, fructosides, fructoses and/or galactoses.  
 Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentagluco-sides and tallow  
 alkyl tetra-, penta-, and hexa-glucosides.

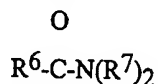
The preferred alkylpolyglycosides have the formula



wherein R<sup>2</sup> is selected from the group consisting of alkyl, alkyl-phenyl, hydroxyalkyl,  
 hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10  
 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t  
 is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from  
 475 about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is  
 preferably derived from glucose. To prepare these compounds, the alcohol or  
 alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of

glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominantly the 2-position.

Fatty acid amide surfactants having the formula:



wherein  $\text{R}^6$  is an alkyl group containing from about 7 to about 21 (preferably from about 9 to about 17) carbon atoms and each  $\text{R}^7$  is selected from the group consisting of hydrogen,  $\text{C}_1\text{-C}_4$  alkyl,  $\text{C}_1\text{-C}_4$  hydroxyalkyl, and  $\text{-(C}^2\text{H}_4\text{O)}_x\text{H}$  where x varies from about 1 to about 3.

Preferred amides are  $\text{C}_8\text{-C}_{20}$  ammonia amides, monoethanolamides, diethanolamides, and isopropanolamides.

Cationic/amphoteric - Non-quaternary, cationic deterative surfactants can also be included in detergent compositions of the present invention. Cationic surfactants useful herein are described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980.

Ampholytic surfactants can be incorporated into the detergent compositions hereof. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35 for examples of ampholytic surfactants. Preferred amphoteric include  $\text{C}_{12}\text{-C}_{18}$  alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and  $\text{C}_6\text{-C}_{12}$  alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy),  $\text{C}_{12}\text{-C}_{18}$  betaines and sulfobetaines ("sultaines"),  $\text{C}_{10}\text{-C}_{18}$  amine oxides, and mixtures thereof.

Polyhydroxy Fatty Acid Amide Surfactant - The detergent compositions hereof may also contain polyhydroxy fatty acid amide surfactant. The polyhydroxy fatty acid amide surfactant component comprises compounds of the structural formula:



wherein:  $\text{R}^1$  is H,  $\text{C}_1\text{-C}_4$  hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably  $\text{C}_1\text{-C}_4$  alkyl, more preferably  $\text{C}_1$  or  $\text{C}_2$  alkyl, most preferably  $\text{C}_1$  alkyl

(i.e., methyl); and  $R^2$  is a  $C_5$ - $C_{31}$  hydrocarbyl, preferably straight chain  $C_7$ - $C_{19}$  alkyl or alkenyl, more preferably straight chain  $C_9$ - $C_{17}$  alkyl or alkenyl, most preferably straight chain  $C_{11}$ - $C_{15}$  alkyl or alkenyl, or mixtures thereof; and Z is a polyhydroxyhydrocarbyl  
 515 having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxyated or propoxyated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z will be a glycityl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose  
 520 corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of  $-CH_2-(CHOH)_n-CH_2OH$ ,  $-CH(CH_2OH)-(CHOH)_{n-1}-CH_2OH$ ,  $-CH_2-(CHOH)_2(CHOH)(CHOH)-CH_2OH$ , and  
 525 alkoxyated derivatives thereof, where n is an integer from 3 to 5, inclusive, and  $R'$  is H or a cyclic or aliphatic monosaccharide. Most preferred are glycityls wherein n is 4, particularly  $-CH_2-(CHOH)_4-CH_2OH$ .

$R'$  can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl.

530  $R^2-CO-N<$  can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriosityl, etc.

Methods for making polyhydroxy fatty acid amides are known in the art. In general,  
 535 they can be made by reacting an alkyl amine with a reducing sugar in a reductive amination reaction to form a corresponding N-alkyl polyhydroxyamine, and then reacting the N-alkyl polyhydroxyamine with a fatty aliphatic ester or triglyceride in a condensation/amidation step to form the N-alkyl, N-polyhydroxy fatty acid amide product. Processes for making compositions containing polyhydroxy fatty acid amides are disclosed, for example, in G.B.  
 540 Patent Specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd., U.S. Patent 2,965,576, issued December 20, 1960 to E. R. Wilson, and U.S. Patent 2,703,798, Anthony M. Schwartz, issued March 8, 1955, and U.S. Patent 1,985,424, issued December 25, 1934 to Piggott, each of which is incorporated herein by reference.

Enzyme Stabilizing System - Enzyme-containing, including but not limited to, liquid  
 545 compositions, herein may comprise from about 0.001% to about 10%, preferably from

about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the detergent composition. See Severson, U.S. 4,537,706 for a review of Borate stabilizers.

Suitable chlorine scavenger anions are widely known and readily available, and, if used, can be salts containing ammonium cations with sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetracetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc., and mixtures thereof can be used if desired.

Enzymes - Suitable enzymes include proteases, amylases, lipases, cellulases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active bleach, detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated into detergent or detergent additive compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as dishware and the like. In practical terms for current commercial preparations, the compositions herein may comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Other Enzymes - enzymes can be included in the present detergent compositions for a variety of purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains from surfaces such as textiles or dishes, for the prevention of refugee dye transfer, for example in laundering, and for fabric restoration. Suitable other

580 enzymes include proteases, lipases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases.

585 "Detersive enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a laundry, hard surface cleaning or personal care detergent composition.

Enzymes are normally incorporated into detergent or detergent additive compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning effective  
590 amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics, dishware and the like. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will  
595 typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. Higher active levels may be desirable in highly concentrated detergent formulations.

600 Peroxidase enzymes may be used in combination with oxygen sources, e.g., percarbonate, perborate, hydrogen peroxide, etc., for "solution bleaching" or prevention of transfer of dyes or pigments removed from substrates during the wash to other substrates present in the wash solution. Known peroxidases include horseradish peroxidase, ligninase, and haloperoxidases such as chloro- or bromo-peroxidase. Peroxidase-containing detergent  
605 compositions are disclosed in WO 89099813 A, October 19, 1989 to Novo and WO 8909813 A to Novo.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to  
610 McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilized by

various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S.  
615 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986,  
Venegas. Enzyme stabilization systems are also described, for example, in U.S. 3,519,570.  
A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO  
9401532 A to Novo.

Amylase - Amylase enzymes include those described in WO95/26397 and in co-  
620 pending application by Novo Nordisk PCT/DK96/00056. These enzymes are incorporated  
into detergent compositions at a level from 0.00018% to 0.060% pure enzyme by weight of  
the total composition, more preferably from 0.00024% to 0.048% pure enzyme by weight  
of total weight composition.

Specific amylase enzymes for use in the detergent compositions of the present  
625 invention therefore include:

- (a)  $\alpha$ -amylases characterised by having a specific activity at least 25% higher than the  
specific activity of Termamyl<sup>®</sup> at a temperature range of 25°C to 55°C and at a pH value in  
the range of 8 to 10, measured by the Phadebas<sup>®</sup>  $\alpha$ -amylase activity assay. Such Phadebas  
<sup>®</sup>  $\alpha$ -amylase activity assay is described at pages 9-10, WO95/26397.
- 630 (b)  $\alpha$ -amylases according (a) comprising the amino sequence shown in the SEQ ID listings  
in the above cited reference. or an  $\alpha$ -amylase being at least 80% homologous with the  
amino acid sequence shown in the SEQ ID listing.
- (c)  $\alpha$ -amylases according (a) comprising the following amino sequence in the N-terminal :  
His-His-Asn-Gly-Thr-Asn-Gly-Thr-Met-Met-Gln-Tyr-Phe-Glu-Trp-Tyr-Leu-Pro-Asn-Asp.
- 635 A polypeptide is considered to be X% homologous to the parent amylase if a  
comparison of the respective amino acid sequences, performed via algorithms, such as the  
one described by Lipman and Pearson in Science 227, 1985, p. 1435, reveals an identity of  
X%
- (d)  $\alpha$ -amylases according (a-c) wherein the  $\alpha$ -amylase is obtainable from an alkalophilic  
640 Bacillus species; and in particular, from any of the strains NCIB 12289, NCIB 12512,  
NCIB 12513 and DSM 935.

In the context of the present invention, the term "obtainable from" is intended not only to  
indicate an amylase produced by a Bacillus strain but also an amylase encoded by a DNA  
sequence isolated from such a Bacillus strain and produced in an host organism  
645 transformed with said DNA sequence.

(e)  $\alpha$ -amylase showing positive immunological cross-reactivity with antibodies raised against an  $\alpha$ -amylase having an amino acid sequence corresponding respectively to those  $\alpha$ -amylases in (a-d).

(f) Variants of the following parent  $\alpha$ -amylases which (i) have one of the amino acid sequences shown in corresponding respectively to those  $\alpha$ -amylases in (a-e), or (ii) displays at least 80% homology with one or more of said amino acid sequences, and/or displays immunological cross-reactivity with an antibody raised against an  $\alpha$ -amylase having one of said amino acid sequences, and/or is encoded by a DNA sequence which hybridizes with the same probe as a DNA sequence encoding an  $\alpha$ -amylase having one of said amino acid sequence; in which variants :

1. at least one amino acid residue of said parent  $\alpha$ -amylase has been deleted; and/or
  2. at least one amino acid residue of said parent  $\alpha$ -amylase has been replaced by a different amino acid residue; and/or
  3. at least one amino acid residue has been inserted relative to said parent  $\alpha$ -amylase;
- said variant having an  $\alpha$ -amylase activity and exhibiting at least one of the following properties relative to said parent  $\alpha$ -amylase : increased thermostability, increased stability towards oxidation, reduced Ca ion dependency, increased stability and/or  $\alpha$ -amylolytic activity at neutral to relatively high pH values, increased  $\alpha$ -amylolytic activity at relatively high temperature and increase or decrease of the isoelectric point (pI) so as to better match the pI value for  $\alpha$ -amylase variant to the pH of the medium.

The preferred amylases of this invention are those described by the following:

- (a)  $\alpha$ -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl<sup>®</sup> at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas<sup>®</sup>  $\alpha$ -amylase activity assay;
- (b)  $\alpha$ -amylase showing positive immunological cross-reactivity with antibodies raised against an  $\alpha$ -amylase having an amino acid sequence corresponding respectively to those  $\alpha$ -amylases in (a); and
- (c) mixtures thereof.

Said variants are described in the patent application PCT/DK96/00056.

Other amylases suitable herein include, for example,  $\alpha$ -amylases described in GB 1,296,839 to Novo; RAPIDASE<sup>®</sup>, International Bio-Synthetics, Inc. and TERMAMYL<sup>®</sup>, Novo. FUNGAMYL<sup>®</sup> from Novo is especially useful.

Engineering of enzymes for improved stability, e.g., oxidative stability, is known. See, for example J. Biological Chem., Vol. 260, No. 11, June 1985, pp. 6518-6521. Certain

680 preferred embodiments of the present compositions can make use of amylases having improved stability in detergents, especially improved oxidative stability as measured against a reference-point of TERMAMYL® in commercial use in 1993. These preferred amylases herein share the characteristic of being "stability-enhanced" amylases, characterized, at a minimum, by a measurable improvement in one or more of: oxidative  
685 stability, e.g., to hydrogen peroxide/tetraacetythylenediamine in buffered solution at pH 9-10; thermal stability, e.g., at common wash temperatures such as about 60°C; or alkaline stability, e.g., at a pH from about 8 to about 11, measured versus the above-identified reference-point amylase. Stability can be measured using any of the art-disclosed technical tests. See, for example, references disclosed in WO 9402597.

690 Stability-enhanced amylases can be obtained from Novo or from Genencor International. One class of highly preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the *Bacillus* amylases, especially the *Bacillus*  $\alpha$ -amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors. Such preferred amylases include (a) an amylase  
695 according to the hereinbefore incorporated WO 9402597, Novo, Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine, preferably threonine, of the methionine residue located in position 197 of the *B. licheniformis* alpha-amylase, known as TERMAMYL®, or the homologous position variation of a similar parent amylase, such as *B. amyloliquefaciens*, *B. subtilis*, or *B. stearothermophilus*; (b)  
700 stability-enhanced amylases as described by Genencor International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C. Mitchinson. Therein it was noted that bleaches in detergents inactivate alpha-amylases but that improved oxidative stability amylases have been made by Genencor from *B. licheniformis* NCIB8061. Methionine (Met) was  
705 identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8, 15, 197, 256, 304, 366 and 438 leading to specific mutants, particularly important being M197L and M197T with the M197T variant being the most stable expressed variant. Stability was measured in CASCADE® and SUNLIGHT®; (c)  
particularly preferred amylases herein include amylase variants having additional  
710 modification in the immediate parent as described in WO 9510603 A and are available from the assignee, Novo, as DURAMYL®. Other particularly preferred oxidative stability enhanced amylase include those described in WO 9418314 to Genencor International and WO 9402597 to Novo. Any other oxidative stability-enhanced amylase can be used, for

example as derived by site-directed mutagenesis from known chimeric, hybrid or simple  
715 mutant parent forms of available amylases. Other preferred enzyme modifications are accessible. See WO 9509909 A to Novo.

Proteases - Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed  
720 and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE® and SAVINASE® from Novo and MAXATASE® from International Bio-Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in  
725 EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985. See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 9318140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A to Novo. Other preferred proteases include those of WO 9510591 A to Procter & Gamble. When desired, a protease having  
730 decreased adsorption and increased hydrolysis is available as described in WO 9507791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 9425583 to Novo.

In more detail, an especially preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is  
735 derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210,  
740 +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in the patent applications of A. Baeck, et al, entitled "Protease-Containing Cleaning Compositions" having US Serial No. 08/322,676, and C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, both filed October 13, 1994.

745 Preferred proteolytic enzymes are also modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303,761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in

European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein, 750  
Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985.

Also preferred proteases are subtilisin enzymes, in particular BPN', that have been modified by mutating the various nucleotide sequences that code for the enzyme, thereby modifying the amino acid sequence of the enzyme. These modified subtilisin enzymes 755  
have decreased adsorption to and increased hydrolysis of an insoluble substrate as compared to the wild-type subtilisin. Also suitable are mutant genes encoding for such BPN' variants.

Preferred BPN' variants comprise wild-type amino acid sequence wherein the wild-type amino acid sequence at one or more of positions 199, 200, 201, 202, 203, 204, 205, 760  
206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 218, 219 or 220 is substituted; wherein the BPN' variant has decreased adsorption to, and increased hydrolysis of, an insoluble substrate as compared to the wild-type subtilisin BPN'. Preferably, the positions having a substituted amino acid are 199, 200, 201, 202, 205, 207, 208, 209, 210, 211, 212, or 215; more preferably, 200, 201, 202, 205 or 207.

765 Preferred protease enzymes for use according to the present invention also include the subtilisin 309 variants. These protease enzymes include several classes of subtilisin 309 variants.

A. Loop Region 6 Substitution Variants - These subtilisin 309 variants have a modified amino acid sequence of subtilisin 309 wild-type amino acid sequence, wherein the 770  
modified amino acid sequence comprises a substitution at one or more of positions 193, 194, 195, 196, 197, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213 or 214; whereby the subtilisin 309 variant has decreased adsorption to, and increased hydrolysis of, an insoluble substrate as compared to the wild-type subtilisin 309. Preferably these proteases have amino acids substituted at 193, 194, 195, 196, 199, 201, 775  
202, 203, 204, 205, 206 or 209; more preferably 194, 195, 196, 199 or 200.

B. Multi-Loop Regions Substitution Variants - These subtilisin 309 variants may also be a modified amino acid sequence of subtilisin 309 wild-type amino acid sequence, wherein the modified amino acid sequence comprises a substitution at one or more positions in one or more of the first, second, third, fourth, or fifth loop regions; whereby the 780  
subtilisin 309 variant has decreased adsorption to, and increased hydrolysis of, an insoluble substrate as compared to the wild-type subtilisin 309.

C. Substitutions at positions other than the loop regions - In addition, one or more substitution of wild-type subtilisin 309 may be made at positions other than positions in the loop regions, for example, at position 74. If the additional substitution to the subtilisin 309 is mad at position 74 alone, the substitution is preferably with Asn, Asp, Glu, Gly, His, Lys, Phe or Pro, preferably His or Asp. However modifications can be made to one or more loop positions as well as position 74, for example residues 97, 99, 101, 102, 105 and 121.

Subtilisin BPN' variants and subtilisin 309 variants are further described in WO 95/29979, WO 95/30010 and WO 95/30011, all of which were published November 9, 1995, all of which are incorporated herein by reference.

Lipases - Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in GB 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open Feb. 24, 1978. Other suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescens* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Further suitable lipases are lipases such as M1 Lipase<sup>R</sup> and Lipomax<sup>R</sup> (Gist-Brocades). Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. LIPOLASE<sup>®</sup> enzyme derived from *Humicola lanuginosa* and commercially available from Novo, see also EP 341,947, is a preferred lipase for use herein. Lipase variants stabilized against peroxidase enzymes are described in WO 9414951 A to Novo. See also WO 9205249 and RD 94359044.

Highly preferred lipases are the D96L lipolytic enzyme variant of the native lipase derived from *Humicola lanuginosa* as described in US Serial No. 08/341,826. (See also patent application WO 92/05249 viz. wherein the native lipase ex *Humicola lanuginosa* aspartic acid (D) residue at position 96 is changed to Leucine (L). According to this nomenclature said substitution of aspartic acid to Leucine in position 96 is shown as : D96L.) Preferably the *Humicola lanuginosa* strain DSM 4106 is used.

In spite of the large number of publications on lipase enzymes, only the lipase derived from *Humicola lanuginosa* and produced in *Aspergillus oryzae* as host has so far found widespread application as additive for fabric washing products. It is available from

Novo Nordisk under the tradename Lipolase™, as noted above. In order to optimize the stain removal performance of Lipolase, Novo Nordisk have made a number of variants. As described in WO 92/05249, the D96L variant of the native *Humicola lanuginosa* lipase improves the lard stain removal efficiency by a factor 4.4 over the wild-type lipase  
820 (enzymes compared in an amount ranging from 0.075 to 2.5 mg protein per liter). Research Disclosure No. 35944 published on March 10, 1994, by Novo Nordisk discloses that the lipase variant (D96L) may be added in an amount corresponding to 0.001-100- mg (5-500,000 LU/liter) lipase variant per liter of wash liquor.

Lipase enzyme is incorporated into the composition in accordance with the invention  
825 at a level of from 50 LU to 8500 LU per liter wash solution. Preferably the variant D96L is present at a level of from 100 LU to 7500 LU per liter of wash solution. More preferably at a level of from 150 LU to 5000 LU per liter of wash solution.

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.  
830 Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor).

Cellulase Enzymes - The laundry detergent compositions according to the present invention may further comprise at least 0.001% by weight, preferably at least about 0.01%,  
835 of a cellulase enzyme. However, an effective amount of cellulase enzyme is sufficient for use in the laundry detergent compositions described herein. The term "an effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics, dishware and the like. The compositions herein will typically comprise from about 0.05%  
840 to about 2%, preferably from about 0.1% to about 1.5% by weight of a commercial enzyme preparation. The cellulase enzymes of the present invention are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. Preferably, the optimum pH of the enzyme-containing composition is between about 7 and about 9.5.

845 U. S. Patent No. 4,435,307, Barbesgaard et al, issued March 6, 1984, discloses cellulase produced from *Humicola insolens*. Examples of other suitable cellulases include those produced by a strain of *Humicola insolens*, *Humicola grisea* var. *thermoidea*, and cellulases produced by a species of *Bacillus* sp. or *Aeromonas* sp. Other useful cellulases are those extracted from the hepatopancreas of the marine mollusc *Dolabella Auricula*

850 *Solander*. Suitable cellulases are also disclosed in the following: GB 2,075,028 A (Novo Industri A/S); GB 2,095,275 A (Kao Soap Co., Ltd.); and Horikoshi et al, U.S. Patent No. 3,844,890 (Rikagaku Kenkyusho). In addition, suitable cellulases and methods for their preparation are described in PCT International Publication Number WO 91/17243, published November 14, 1991, by Novo Nordisk A/S.

855 Cellulases are known in the art and can be obtained from suppliers under the tradenames: Celluzyme®, Endolase®, and Carezyme®.

For industrial production of the cellulases herein it is preferred that recombinant DNA techniques be employed. However other techniques involving adjustments of fermentations or mutation of the microorganisms involved can be employed to ensure  
860 overproduction of the desired enzymatic activities. Such methods and techniques are known in the art and may readily be carried out by persons skilled in the art.

Perfumes - Perfumes and perfumery ingredients useful in the present compositions and processes comprise a wide variety of natural and synthetic chemical ingredients, including, but not limited to, aldehydes, ketones, esters, and the like. Also included are  
865 various natural extracts and essences which can comprise complex mixtures of ingredients, such as orange oil, lemon oil, rose extract, lavender, musk, patchouli, balsamic essence, sandalwood oil, pine oil, cedar, and the like. Finished perfumes can comprise extremely complex mixtures of such ingredients. Finished perfumes typically comprise from about 0.01% to about 4%, by weight, of the detergent compositions herein, and individual  
870 perfumery ingredients can comprise from about 0.0001% to about 90% of a finished perfume composition.

Material Care Agents - The present compositions may optionally contain as corrosion inhibitors and/or anti-tarnish aids one or more material care agents such as silicates. Material care agents include bismuth salts, transition metal salts such as those of  
875 manganese, certain types of paraffin, triazoles, pyrazoles, thiols, mercaptans, aluminium fatty acid salts, and mixtures thereof and are preferably incorporated at low levels, e.g., from about 0.01% to about 5% of the composition. A preferred paraffin oil is a predominantly branched aliphatic hydrocarbon comprising from about 20 to about 50 carbon atoms with a ratio of cyclic to noncyclic hydrocarbons of about 32 to 68 sold by  
880 Wintershall, Salzbergen, Germany as WINOG 70®. Bi(NO<sub>3</sub>)<sub>3</sub> may be added. Other corrosion inhibitors are illustrated by benzotriazole, thiols including thionaphtol and thioanthranol, and finely divided aluminium fatty acid salts. All such materials will generally be used judiciously so as to avoid producing spots or films on glassware or

compromising the bleaching action of the compositions. For this reason, it may be  
885 preferred to formulate without mercaptan anti-tarnishes which are quite strongly bleach-  
reactive or common fatty carboxylic acids which precipitate with calcium.

Chelating Agents - The detergent compositions herein may also optionally contain  
one or more iron and/or manganese chelating agents. Such chelating agents can be selected  
from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-  
890 substituted aromatic chelating agents and mixtures therein, all as hereinafter defined.  
Without intending to be bound by theory, it is believed that the benefit of these materials is  
due in part to their exceptional ability to remove iron and manganese ions from washing  
solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include  
895 ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates,  
ethylenediamine tetrapropionates, triethylenetetraaminehexacetates,  
diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and  
substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions  
900 of the invention when at least low levels of total phosphorus are permitted in detergent  
compositions, and include ethylenediaminetetrakis (methylenephosphonates) as  
DEQUEST. Preferred, these amino phosphonates do not contain alkyl or alkenyl groups  
with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the  
905 compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al.  
Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-  
dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate  
("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3,  
910 1987, to Hartman and Perkins.

The compositions herein may also contain water-soluble methyl glycine diacetic acid  
(MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble  
builders such as zeolites, layered silicates and the like.

If utilized, these chelating agents will generally comprise from about 0.1% to about  
915 15% by weight of the detergent compositions herein. More preferably, if utilized, the  
chelating agents will comprise from about 0.1% to about 3.0% by weight of such  
compositions.

Polymeric Dispersing Agents - Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued march 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium

and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also  
955 describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Other polymeric materials which can be included are polypropylene glycol (PPG),  
960 propylene glycol (PG), and polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in  
965 conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq. Chemically, these materials comprise  
970 polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula  $-(CH_2CH_2O)_m(CH_2)_nCH_3$  wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can comprise from about 0.05% to about  
975 10%, by weight, of the compositions herein.

The levels of these dispersants used can range from about 0.1% to about 10%, typically from about 0.4% to about 5%, by weight. These dispersants can be synthesized following the methods outline in US. Patent No. 4,664,848, or other ways known to those skilled in the art.

980 Dye Fixative Materials - optionally but preferred for use herein are selected dye fixative materials which do not form precipitates with anionic surfactant.

The selected dye fixatives useful herein may be in the form of unpolymerized materials, oligomers or polymers. Moreover, the preferred dye fixatives useful herein are cationic. The dye fixative component of the compositions herein will generally comprise  
985 from about 0.1% to 5% by the weight of the composition. More preferably, such dye

fixative materials will comprise from about 0.5% to 4% by weight of the compositions, most preferably from about 1% to 3%. Such concentrations should be sufficient to provide from about 10 to 100 ppm of the dye fixative in the aqueous washing solutions formed from the laundry detergent compositions herein. More preferably from about 20 to 60  
990 ppm of the dye fixative will be delivered to the aqueous washing solution, most preferably about 50 ppm.

The non-precipitating dye fixatives useful herein include a number that are commercially marketed by CLARIANT Corporation under the Sandofix<sup>®</sup>, Sandolec<sup>®</sup> and Polymer VRN<sup>®</sup> tradenames. These include, for example, Sandofix SWE<sup>®</sup>, Sandofix WA  
995 <sup>®</sup>, Sandolec CT<sup>®</sup>, Sandolec CS<sup>®</sup>, Sandolec C1<sup>®</sup>, Sandolec CF<sup>®</sup>, Sandolec WA<sup>®</sup> and Polymer VRN<sup>®</sup>. Other suitable dye fixatives are marketed by Ciba-Geigy Corporation under the tradename Cassofix FRN-300<sup>®</sup> and by Hoechst Celanese Corporation under the tradename Tinofix EW<sup>®</sup>.

Builders - Detergent builders can optionally but preferably be included in the  
1000 compositions herein, for example to assist in controlling mineral, especially Ca and/or Mg, hardness in wash water or to assist in the removal of particulate soils from surfaces. Builder level can vary widely depending upon end use and physical form of the composition. Built detergents typically comprise at least about 1% builder. Liquid formulations typically comprise about 5% to about 50%, more typically 5% to 35% of  
1005 builder. Lower or higher levels of builders are not excluded. For example, certain detergent additive or high-surfactant formulations can be unbuilt.

Suitable builders herein can be selected from the group consisting of phosphates and polyphosphates, especially the sodium salts; silicates including water-soluble and hydrous solid types and including those having chain-, layer-, or three-dimensional- structure as  
1010 well as amorphous-solid or non-structured-liquid types; carbonates, bicarbonates, sesquicarbonates and carbonate minerals other than sodium carbonate or sesquicarbonate; aluminosilicates; organic mono-, di-, tri-, and tetracarboxylates especially water-soluble nonsurfactant carboxylates in acid, sodium, potassium or alkanolammonium salt form, as well as oligomeric or water-soluble low molecular weight polymer carboxylates including  
1015 aliphatic and aromatic types; and phytic acid. These may be complemented by borates, e.g., for pH-buffering purposes, or by sulfates, especially sodium sulfate and any other fillers or carriers which may be important to the engineering of stable surfactant and/or builder-containing detergent compositions.

Builder mixtures, sometimes termed "builder systems" can be used and typically  
1020 comprise two or more conventional builders, optionally complemented by chelants, pH-  
buffers or fillers, though these latter materials are generally accounted for separately when  
describing quantities of materials herein.

P-containing detergent builders often preferred where permitted by legislation  
include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of  
1025 polyphosphates exemplified by the tripolyphosphates, pyrophosphates, glassy polymeric  
meta-phosphates; and phosphonates.

Suitable silicate builders include alkali metal silicates, particularly those liquids and  
solids having a  $\text{SiO}_2:\text{Na}_2\text{O}$  ratio in the range 1.6:1 to 3.2:1, including, particularly for  
automatic dishwashing purposes, solid hydrous 2-ratio silicates marketed by PQ Corp.  
1030 under the tradename BRITESIL<sup>®</sup>, e.g., BRITESIL H<sub>2</sub>O; and layered silicates, e.g., those  
described in U.S. 4,664,839, May 12, 1987, H. P. Rieck. See preparative methods in  
German DE-A-3,417,649 and DE-A-3,742,043.

Also suitable for use herein are synthesized crystalline ion exchange materials or  
hydrates thereof as taught in U.S. 5,427,711, Sakaguchi et al, June 27, 1995.

1035 Suitable carbonate builders include alkaline earth and alkali metal carbonates as  
disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are especially useful in granular detergents, but can also be  
incorporated in liquids. Suitable for the present purposes are those having empirical  
formula:  $[\text{M}_z(\text{AlO}_2)_z(\text{SiO}_2)_v] \cdot x\text{H}_2\text{O}$  wherein z and v are integers of at least 6, the molar  
1040 ratio of z to v is in the range from 1.0 to 0.5, and x is an integer from 15 to 264.

Aluminosilicates can be crystalline or amorphous, naturally-occurring or synthetically  
derived. An aluminosilicate production method is in U.S. 3,985,669, Krummel, et al,  
October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials  
are available as Zeolite A, Zeolite P (B), Zeolite X and, to whatever extent this differs from  
1045 Zeolite P, the so-called Zeolite MAP.

Suitable organic detergent builders include polycarboxylate compounds, including  
water-soluble nonsurfactant dicarboxylates and tricarboxylates. More typically builder  
polycarboxylates have a plurality of carboxylate groups, preferably at least 3 carboxylates.  
Carboxylate builders can be formulated in acid, partially neutral, neutral or overbased form.  
1050 When in salt form, alkali metals, such as sodium, potassium, and lithium, or  
alkanolammonium salts are preferred. Polycarboxylate builders include the ether  
polycarboxylates, such as oxydisuccinate, see Berg, U.S. 3,128,287, April 7, 1964, and

Lamberti et al, U.S. 3,635,830, January 18, 1972; "TMS/TDS" builders of U.S. 4,663,071, Bush et al, May 5, 1987; and other ether carboxylates including cyclic and alicyclic  
 1055 compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other suitable builders are the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether; 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid; carboxymethyloxysuccinic acid; the various alkali metal, ammonium and  
 1060 substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid; as well as mellitic acid, succinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Oxydisuccinates are also especially useful in such compositions and combinations.

Certain deterative surfactants or their short-chain homologs also have a builder action.  
 1065 For unambiguous formula accounting purposes, when they have surfactant capability, these materials are summed up as deterative surfactants. Preferred types for builder functionality are illustrated by: 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. 4,566,984, Bush, January 28, 1986. Succinic acid builders include the C<sub>5</sub>-C<sub>20</sub> alkyl and alkenyl succinic acids and salts thereof. Succinate builders also include:  
 1070 laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Lauryl-succinates are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986. Fatty acids, e.g., C<sub>12</sub>-C<sub>18</sub> monocarboxylic acids, can also be incorporated into the compositions as surfactant/builder materials alone or in combination with the aforementioned builders,  
 1075 especially citrate and/or the succinate builders, to provide additional builder activity. Other suitable polycarboxylates are disclosed in U.S. 4,144,226, Crutchfield et al, March 13, 1979 and in U.S. 3,308,067, Diehl, March 7, 1967. See also Diehl, U.S. 3,723,322.

Other types of inorganic builder materials which can be used have the formula (M<sub>x</sub>)<sub>i</sub> Ca<sub>y</sub> (CO<sub>3</sub>)<sub>z</sub> wherein x and i are integers from 1 to 15, y is an integer from 1 to 10, z is an  
 1080 integer from 2 to 25, M<sub>i</sub> are cations, at least one of which is a water-soluble, and the equation  $\sum_i = 1-15(x_i \text{ multiplied by the valence of } M_i) + 2y = 2z$  is satisfied such that the formula has a neutral or "balanced" charge. These builders are referred to herein as "Mineral Builders".

Polymeric Soil Release Agent - Known polymeric soil release agents, hereinafter  
 1085 "SRA" or "SRA's", can optionally be employed in the present detergent compositions. If

utilized, SRA's will generally comprise from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight, of the composition.

1090 SRA's can include a variety of charged, e.g., anionic or even cationic (see U.S. 4,956,447), as well as noncharged monomer units and structures may be linear, branched or even star-shaped. They may include capping moieties which are especially effective in controlling molecular weight or altering the physical or surface-active properties. Structures and charge distributions may be tailored for application to different fiber or textile types and for varied detergent or detergent additive products.

1095 Suitable SRA's include a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units, for example as described in U.S. 4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselink. See U.S. 4,711,730, December 8, 1987 to Gosselink et al, for examples of those produced by transesterification/ oligomerization of poly(ethyleneglycol) methyl ether, DMT, PG and poly(ethyleneglycol) ("PEG"). Partly- and fully- anionic-end-capped  
1100 oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink, such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; the nonionic-capped block polyester oligomeric compounds of U.S. 4,702,857, October 27, 1987 to Gosselink, for example produced from DMT, Me-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-  
1105 sulfoisophthalate; and the anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al.

SRA's also include simple copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, see U.S. 3,959,230 to Hays, May 25, 1976 and U.S. 3,893,929 to Basadur, July 8, 1975; cellulosic  
1110 derivatives such as the hydroxyether cellulosic polymers available as METHOCEL from Dow; and the C<sub>1</sub>-C<sub>4</sub> alkylcelluloses and C<sub>4</sub> hydroxyalkyl celluloses; see U.S. 4,000,093, December 28, 1976 to Nicol, et al. Suitable SRA's characterised by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C<sub>1</sub>-C<sub>6</sub> vinyl esters, preferably poly(vinyl acetate), grafted onto polyalkylene oxide backbones. See  
1115 European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Commercially available examples include SOKALAN SRA's such as SOKALAN HP-22, available from BASF, Germany. Other SRA's are polyesters with repeat units containing 10-15% by weight of ethylene terephthalate together with 90-80% by weight of polyoxyethylene terephthalate, derived from a polyoxyethylene glycol of average molecular

1120 weight 300-5,000. Commercial examples include ZELCON 5126 from Dupont and MILEASE T from ICI.

U.S. 5,415,807, Gosselink, Pan, Kellett and Hall, issued May 16, 1995. Suitable monomers for the above SRA include Na 2-(2-hydroxyethoxy)-ethanesulfonate, DMT, Na-dimethyl 5-sulfoisophthalate, EG and PG.

1125 Additional classes of SRA's include (I) nonionic terephthalates using diisocyanate coupling agents to link up polymeric ester structures, see U.S. 4,201,824, Violland et al. and U.S. 4,240,918 Lagasse et al; (II) SRA's with carboxylate terminal groups made by adding trimellitic anhydride to known SRA's to convert terminal hydroxyl groups to trimellitate esters. With a proper selection of catalyst, the trimellitic anhydride forms  
1130 linkages to the terminals of the polymer through an ester of the isolated carboxylic acid of trimellitic anhydride rather than by opening of the anhydride linkage. Either nonionic or anionic SRA's may be used as starting materials as long as they have hydroxyl terminal groups which may be esterified. See U.S. 4,525,524 Tung et al.; (III) anionic terephthalate-based SRA's of the urethane-linked variety, see U.S. 4,201,824, Violland et al; (IV)  
1135 poly(vinyl caprolactam) and related co-polymers with monomers such as vinyl pyrrolidone and/or dimethylaminoethyl methacrylate, including both nonionic and cationic polymers, see U.S. 4,579,681, Ruppert et al.; (V) graft copolymers, in addition to the SOKALAN types from BASF made, by grafting acrylic monomers on to sulfonated polyesters; these SRA's assertedly have soil release and anti-redeposition activity similar to known cellulose  
1140 ethers: see EP 279,134 A, 1988, to Rhone-Poulenc Chemie; (VI) grafts of vinyl monomers such as acrylic acid and vinyl acetate on to proteins such as caseins, see EP 457,205 A to BASF (1991); (VII) polyester-polyamide SRA's prepared by condensing adipic acid, caprolactam, and polyethylene glycol, especially for treating polyamide fabrics, see Bevan et al, DE 2,335,044 to Unilever N. V., 1974. Other useful SRA's are described in U.S.  
1145 Patents 4,240,918, 4,787,989, 4,525,524 and 4,877,896.

Brightener - Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.01% to about 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are  
1150 not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed

in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

- 1155        Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, the 2-(4-styryl-phenyl)-2H-naptho[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the aminocoumarins. See also U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton.

- 1160        Dye Transfer Inhibiting Agents - The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

The N-O group can be represented by the following general structures:

- 1175        The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which has an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

- 1180        Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.
- 1185

The present invention compositions also may employ a poly-vinyl-pyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

The detergent compositions herein may also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from about 0.01% to 1% by weight of such optical brighteners.

Particular brightener species, commercially marketed under the tradenames Tinopal-UNPA-GX, Tinopal AMS-GX, and Tinopal 5BM-GX by Ciba-Geigy Corporation, are also included. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

Suds Suppressors - Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in U.S. 4,489,455 and 4,489,574 and in front-loading European-style washing machines.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The detergent compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C<sub>18</sub>-C<sub>40</sub> ketones (e.g., stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkyldiamine chlortriazines

1225 formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al.

1230 Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethyl-siloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al and European Patent Application No. 89307851.9, published February 7, 1990, by Starch, M. S.

1235 Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

1240 Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672, Bartolotta et al, and in U.S. Patent 4,652,392, Baginski et al, issued March 24, 1987.

1245 Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils, such as the silicones disclosed in U.S. 4,798,679, 4,075,118 and EP 150,872. The secondary alcohols include the C<sub>6</sub>-C<sub>16</sub> alkyl alcohols having a C<sub>1</sub>-C<sub>16</sub> chain. A preferred alcohol is 2-butyl octanol, which is available from Condea under the trademark ISOFOL 12. Mixtures of secondary alcohols are available under the trademark ISALCHEM 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol + silicone at a weight ratio of 1:5 to 5:1.

1250 Alkoxyated Polycarboxylates - Alkoxyated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated herein by reference. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula  $-(CH_2CH_2O)_m(CH_2)_nCH_3$  wherein m is 2-3 and n is 6-12. The side-chains are

1255 ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure.  
The molecular weight can vary, but is typically in the range of about 2000 to about 50,000.  
Such alkoxyated polycarboxylates can comprise from about 0.05% to about 10%, by  
weight, of the compositions herein.

Fabric Softeners - Various through-the-wash fabric softeners, especially the  
1260 impalpable smectite clays of U.S. Patent 4,062,647, Storm and Nirschl, issued December  
13, 1977, as well as other softener clays known in the art, can optionally be used typically  
at levels of from about 0.5% to about 10% by weight in the present compositions to provide  
fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in  
combination with amine and cationic softeners as disclosed, for example, in U.S. Patent  
1265 4,375,416, Crisp et al, March 1, 1983 and U.S. Patent 4,291,071, Harris et al, issued  
September 22, 1981.

The compositions of this invention can be used to form aqueous washing solutions for  
use in the laundering of fabrics. Generally, an effective amount of such compositions is  
1270 added to water, preferably in a conventional fabric laundering automatic washing machine,  
to form such aqueous laundering solutions. The aqueous washing solution so formed is  
then contacted, preferably under agitation, with the fabrics to be laundered therewith.

An effective amount of the liquid detergent compositions herein added to water to  
form aqueous laundering solutions can comprise amounts sufficient to form from about 500  
1275 to 7,000 ppm of composition in aqueous solution. More preferably, from about 800 to  
3,000 ppm of the detergent compositions herein will be provided in aqueous washing  
solution.

The following examples are illustrative of the present invention, but are not meant to  
limit or otherwise define its scope. All parts, percentages and ratios used herein are  
1280 expressed as percent weight unless otherwise specified.

In the following Examples all levels are quoted as % by weight of the composition.

#### EXAMPLE I

The following non-limiting examples are within the scope of the present invention.

Example	A	B	C	D	E	F
C12-15E2.5S	21	21	20.2	22.7	22.7	13.6
C12LAS	-	-	-	-	-	9.1
C12-14 glucosamide	4	4	2.5	-	-	-

C12-14EO7	4.5	4.5	-	-	-	-
C12-15EO9	-	-	0.6	0.6	0.6	0.6
C8-10 amidopropylamine	1.3	1.3	-	-	-	-
C10 amidopropylamine	-	-	1.3	1.3	1.3	1.3
citric acid	1	3	5	1	2.5	1
C12/14 fatty acid	-	-	10	10	8	10
palm kernal fatty acid	8	5.4	-	-	-	-
rapeseed fatty acid	8	5.4	-	-	-	-
protease	0.6	0.6	0.9	0.9	0.9	0.9
lipase	0.07	0.07	0.08	0.08	0.08	0.08
amylase	0.18	0.18	0.15	0.15	0.15	0.15
cellulase	0.03	0.03	0.05	0.05	0.05	0.05
endolase	0.2	0.2	-	-	-	-
brightener	0.15	0.15	0.15	0.15	0.15	0.15
polymer A	0.66	0.66	0.6	0.6	0.6	0.6
polymer B	-	-	1.2	1.2	1.2	1.2
Polyamine-polyamide	2	-	1	1	-	-
Polyethoxylated- polyamines	-	1	2	-	-	-
soil release agent	-	-	0.1	0.1	0.1	0.1
ethanol	0.7	0.7	0.54	0.54	0.54	0.54
1,2-propanediol	4	4	4	4	4	4
MEA	0.7	0.7	0.5	0.5	0.5	0.5
NaOH	2.8	2.8	7	7	7	7
boric acid	2	2	-	-	-	-
borax	-	-	2.5	2.5	2.5	2.5
suds supressor	-	-	0.1	0.1	0.1	0.1
PDMS	0.2	0.2	-	-	-	-
perfume	0.5	0.5	0.75	0.75	0.75	0.75
dye	-	-	0.04	0.04	0.04	0.04
water	balance	balance	balance	balance	balance	balance

Example Number	G	H	I	J
C12-15E2.5S	18.12	18.25	22.65	22.65
C12LAS	4.5	-	-	-
C12-15EO9	0.6	5	0.6	0.6
C10 amidopropylamine	1.3	1.3	1.3	1.3
citric acid	1	1	1	1
C12/14 fatty acid	10	10	10	10
Quaternary Surfactant	0.5	1	5	-
oleic acid	-	-	-	2.5
protease	0.9	0.9	0.9	0.9
lipase	0.08	0.08	0.08	0.08
amylase	0.15	0.15	0.15	0.15
cellulase	0.05	0.05	0.05	0.05
brightener	0.15	0.15	0.15	0.15
polymer A	0.6	0.6	0.3	0.6
polymer B	1.2	1.2	0.6	1.2
soil release agent	0.1	0.1	0.1	0.1
ethanol	0.54	0.54	0.54	0.54
1,2-propanediol	4	4	4	4
MEA	0.48	0.48	0.48	0.48
NaOH	7	7	7	7
borax	2.5	2.5	2.5	2.5
suds supressor	0.1	0.1	0.1	0.1
perfume	0.75	0.75	0.75	0.75
dye	0.04	0.04	0.04	0.04
water	balance	balance	balance	balance

1285

Example Number	K	L	M
C12-15E2.5S	27.65	22.65	22.65
C12-15EO9	0.6	0.6	0.6
C10 amidopropylamine	1.3	1.3	1.3
citric acid	1	1	1

C12/14 fatty acid	7.5	5	10
protease	0.9	0.9	0.9
lipase	0.08	0.08	0.08
amylase	0.15	0.15	0.15
cellulase	0.05	0.05	0.05
brightener	0.15	0.15	0.15
polymer A	0.6	0.6	0.6
polymer B	1.2	1.2	1.2
soil release agent	0.1	0.1	0.1
ethanol	0.54	0.54	0.54
1,2-propanediol	4	4	4
MEA	0.48	0.48	0.48
NaOH	7	7	7
borax	2.5	-	2.5
suds supressor	0.1	0.1	0.1
perfume	0.75	0.75	0.75
dye	0.04	0.04	0.04
water	balance	balance	balance

Polymer A are modified polyamines of PEI (MW = 182) with average degree of ethoxylation = 15

Polymer B are modified polyamines of PEI (MW = 600) with average degree of ethoxylation = 20

1290 Monoethanolamine = (MEA)

Quaternary Surfactant is selected from one or more of the following: lauryl trimethyl ammonium chloride, myristyl trimethyl ammonium chloride, palmityl trimethyl ammonium chloride, coconut trimethylammonium chloride, coconut trimethylammonium methylsulfate, coconut dimethyl-monohydroxyethyl-ammonium chloride, coconut

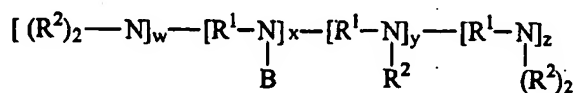
1295 dimethyl-monohydroxyethylammonium methylsulfate, steryl dimethyl-monohydroxyethylammonium chloride, steryl dimethylmonohydroxy-ethylammonium methylsulfate, di-C<sub>12</sub>-C<sub>14</sub> alkyl dimethyl ammonium chloride.

The polyamide-polyamines herein are commercially marketed under the tradenames:

Kymene<sup>®</sup>, Kymene 557H<sup>®</sup>, Kymene 557LX<sup>®</sup>, Reten<sup>®</sup>, and Cartaretin<sup>®</sup>.

**WHAT IS CLAIMED IS:**

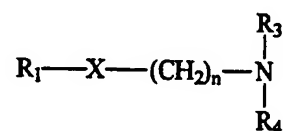
1. A gel laundry detergent composition comprising, by weight of the composition:
  - a) from 15% to 40% of an anionic surfactant component which is characterized in that the anionic surfactant component comprises, by weight of the composition:
    - (i) from 5% to 25% of alkyl polyethoxylate sulfates wherein the alkyl group contains from 10 to 22 carbon atoms and the polyethoxylate chain contains from 0.5 to 15, preferably from 0.5 to 5, more preferably from 0.5 to 4, ethylene oxide moieties; and
    - (ii) from 5% to 20% of fatty acids; and
  - b) and one or more of the following ingredients: deterative amines, modified polyamines, polyamide-polyamines, polyethoxylated-polyamine polymers, quaternary ammonium surfactants, suitable electrolyte or acid equivalents thereof, and mixtures thereof.
2. A composition according to Claim 1 wherein the detergent composition additionally comprises adjunct ingredients selected from the group consisting of non-citrate builders, optical brighteners, soil release polymers, dye transfer inhibitors, polymeric dispersing agents, enzymes, suds suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, antiredeposition agents, antifading agent, dye fixative agents, prill/fuzzing reducing agents, and mixtures thereof.
3. A composition according to Claim 1 wherein said ingredient (b) comprises from 2% to 6% of an electrolyte.
4. A composition according to Claim 3 wherein said electrolyte is a citric acid.
5. A composition according to Claim 1 wherein said ingredient (b) comprises at least 0.05%, by weight, of a water-soluble or dispersible, modified polyamine agent, said agent comprises a polyamine backbone corresponding to the formula:



wherein each  $R^1$  is independently  $C_2$ - $C_5$  alkylene, alkenylene or arylene; each  $R^2$  is independently H, or a moiety of formula  $OH[(CH_2)_xO]_n$ , wherein x is

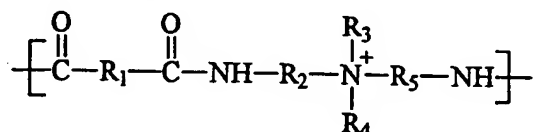
from 1 to 8 and n is from 10 to 50; w is 0 or 1; x+y+z is from 5 to 30; and B represents a continuation of this structure by branching; and wherein said polyamine before alkylation has an average molecular weight of from 300 to 1,200.

6. A composition according to Claim 1 wherein the ingredient (b) comprises from 0.1% to 10%, by weight, of a deterative amine; wherein said amine is of the formula:



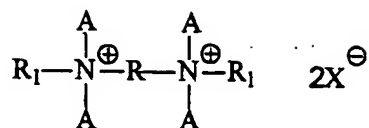
wherein R<sub>1</sub> is a C<sub>6</sub>-C<sub>12</sub> alkyl group; n is from 2 to 4, X is a bridging group which is selected from NH, CONH, COO, or O or X can be absent; and R<sub>3</sub> and R<sub>4</sub> are individually selected from H, C<sub>1</sub>-C<sub>4</sub> alkyl, or (CH<sub>2</sub>-CH<sub>2</sub>-O(R<sub>5</sub>)) wherein R<sub>5</sub> is H or methyl.

7. A composition according to Claim 1 wherein the ingredient (b) comprises from 0.1% to 8% by the weight of the composition of polyamide-polyamine which have repeating, substituted amido-amine units which correspond to the general structure as follows:

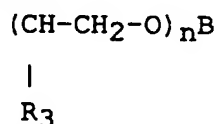


wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>5</sub> are each independently C<sub>1-4</sub> alkylene, C<sub>1-4</sub> alkarylene or arylen; R<sub>3</sub> is H, epichlorohydrin, an azetidinium group, an epoxypropyl group or a dimethylaminohydroxypropyl group; R<sub>4</sub> can be H, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkaryl, aryl, or any of the foregoing groups condensed with C<sub>1-4</sub> alkylene oxide.

8. A composition according to Claim 1 wherein the ingredient (b) comprises from 0.1% to 10%, by the weight of the composition, of polyethoxylated-polyamine polymers which are alkoxyated quaternary diamines of the general formula:

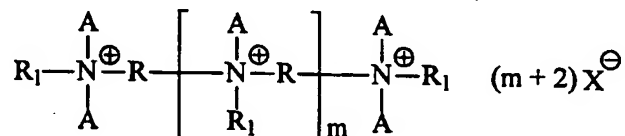


where R is selected from linear or branched C<sub>2</sub>-C<sub>12</sub> alkylene, C<sub>3</sub>-C<sub>12</sub> hydroxy-alkylene, C<sub>4</sub>-C<sub>12</sub> dihydroxyalkylene, C<sub>8</sub>-C<sub>12</sub> dialkylarylene, [(CH<sub>2</sub>CH<sub>2</sub>O)<sub>q</sub> CH<sub>2</sub>CH<sub>2</sub>]- and -CH<sub>2</sub>CH(OH)CH<sub>2</sub>O-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>q</sub>CH<sub>2</sub>CH(OH)CH<sub>2</sub>]- where q is from 1 to 100; each R<sub>1</sub> is independently selected from C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>7</sub>-C<sub>12</sub> alkylaryl, or A; A is of the formula:

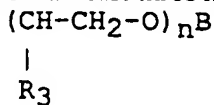


where R<sub>3</sub> is selected from H or C<sub>1</sub>-C<sub>3</sub> alkyl, n is from 5 to 100, and B is selected from H, C<sub>1</sub>-C<sub>4</sub> alkyl, acetyl, or benzoyl; X is a water soluble anion.

9. A composition according to Claim 1 wherein the ingredient (b) comprises from 0.1% to 10%, by the weight of the composition, of polyethoxylated-polyamine polymers which are alkoxyated quaternary diamines of the general formula:

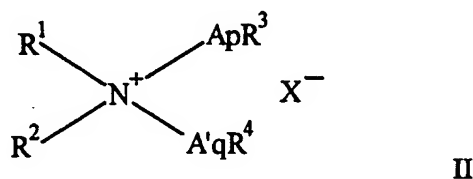
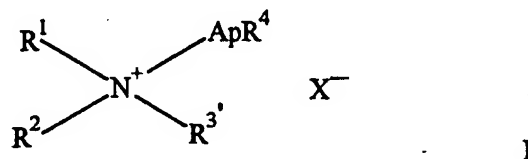


where R is selected from linear or branched C<sub>2</sub>-C<sub>12</sub> alkylene, C<sub>3</sub>-C<sub>12</sub> hydroxy-alkylene, C<sub>4</sub>-C<sub>12</sub> dihydroxyalkylene, C<sub>8</sub>-C<sub>12</sub> dialkylarylene, [(CH<sub>2</sub>CH<sub>2</sub>O)<sub>q</sub> CH<sub>2</sub>CH<sub>2</sub>]- and -CH<sub>2</sub>CH(OH)CH<sub>2</sub>O-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>q</sub>CH<sub>2</sub>CH(OH)CH<sub>2</sub>]- where q is from 1 to 100; each R<sub>1</sub>, if present, is independently selected from C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>7</sub>-C<sub>12</sub> alkylaryl, or A; and wherein at least three nitrogens must be quaternized; A is of the formula:



where R<sub>3</sub> is selected from H or C<sub>1</sub>-C<sub>3</sub> alkyl, n is from 5 to 100 and B is selected from H, C<sub>1</sub>-C<sub>4</sub> alkyl, acetyl, or benzoyl; m is from 0 to 4, and X is a water soluble anion.

10. A composition according to Claim 1 wherein the ingredient (b) comprises from 1% to 6%, by the weight of the composition, of a quaternary ammonium surfactant of the general formula:



wherein  $\text{R}^1$  is an alkyl or alkenyl moiety containing from 8 to 18 carbon atoms;  $\text{R}^2$  and  $\text{R}^{3'}$  are each independently alkyl groups containing from one to about three carbon atoms;  $\text{R}^3$  and  $\text{R}^4$  can vary independently and are selected from hydrogen, methyl and ethyl;  $\text{X}^-$  is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, to provide electrical neutrality; A is selected from  $\text{C}_1$ - $\text{C}_4$  alkoxy; and for formula I, p is from 2 to 30; and for formula II, p is from 1 to 30 and q is from 1 to 30.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/15281

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D17/00 C11D1/29 C11D1/62 C11D1/65 C11D1/37  
C11D3/37

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	WO 98 29530 A (PROCTER & GAMBLE) 9 July 1998 see page 3, paragraph 3 - page 4, paragraph 2; claim 1	1, 2, 7
P, A	WO 97 42287 A (PROCTER & GAMBLE) 13 November 1997 see page 2, paragraph 3; claims 1-3, 6, 7, 9	1, 2, 4-10
A	GB 2 280 450 A (PROCTER & GAMBLE) 1 February 1995 see claim 1	1

☐ Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

19 October 1998

Date of mailing of the international search report

02/11/1998

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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